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(54) **A method of modifying starch**

(57) A method is described, in which the starch-modification reaction is carried out by the centrifuging of the reagents (starch and modification agents) within a cylindrical turbo-reactor (1) having a bladed rotor, with the creation of a thin, tubular, dynamic, fluid layer.

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Description

The present invention relates, in general, to a method for the continuous chemical modification of starch.

The great interest shown by many branches of industry in the availability of raw materials based on modified starches, and consequently in methods for the chemical modification of starch which can be carried out on an industrial scale, is well known.

Thus, for example, it is known that the textile and paper industries have a particular interest in hydrolytic treatments of starch to produce starch sizing of a suitably low viscosity.

It is also known that suitable hydrolytic treatment of starch, again on an industrial scale, can produce dextrin, maltose and glucose, which have other important technical uses.

Further chemical modifications of starch which are of industrial interest are esterification and etherification reactions which give rise to products such as starch acetate, starch hydroxyethylate, starch hydroxypropylate and other simple or mixed ethers and esters. As is well known, these products are widely used in the food industry as gelling or thickening agents, in the textile industry as sizing, and in the paper industry for improving printability, surface strength and the solvent-resistance of paper.

The methods of the prior art for the chemical modification of starch on an industrial scale are generally based on batch processing of starch in an aqueous solution or in the presence of a large quantity of water.

In fact, according to the prevalent teaching of the prior art, this is the only method in which optimal contact between the hydroxylic groups of the starch and the agents used for its chemical modification can be achieved in an industrially advantageous and valuable manner.

However, although, on the one hand the aforementioned technical teaching enables a chemically modified and industrially acceptable starch to be produced, on the other hand, it has the recognized disadvantage of producing enormous quantities of aqueous reflux, the disposal of which results in a considerable burden on production and running costs.

Moreover, the methods of the prior art have to be carried out discontinuously (in batches) which, as is well known, has an adverse effect on their control and on the overall economy of the method.

The technical problem upon which the present invention is based is that of providing a method for the chemical modification of starch which avoids the problems listed above with reference to the methods of the prior art.

This problem is solved, according to the invention, by a method for the continuous chemical modification of starch, characterized in that it comprises the steps of:

- supplying a continuous flow of starch in powder form having a moisture content of between 9 and 25% into a turbo-reactor comprising a cylindrical, tubular body with a horizontal axis, having openings for the admission of agents and for the outlet of the final product, a bladed rotor supported for rotation in the cylindrical, tubular body, in which it is rotated at speeds within the range of from 300 to 1500 revolutions/minute, so as to disperse the continuous flow of starch into a flow of starch particles and, possibly a heating or cooling jacket for bringing the internal wall of the tubular body to a predetermined temperature,
- supplying at least one continuous, substantially aeriform flow of at least one starch-modification agent into the turbo-reactor, with the same direction of flow as the starch flow,
- centrifuging the starch particles and the modification agent against the internal wall of the turbo-reactor, forming a thin, tubular, dynamic, highly turbulent, fluid layer in which the starch particles and the modification agent are kept mechanically in intimate contact by the blades of the bladed rotor, and
- reacting the starch and the agent in the thin layer whilst it advances substantially in contact with the internal wall towards the opening of the turbo-reactor.

If one or more of the starch-modification agents are available in a liquid state, they may be supplied to the turbo-reactor as they are since, as soon as they are admitted thereto, the bladed rotor effectively nebulizes and centrifuges them, consequently ensuring that they are introduced into the thin, tubular, fluid layer of starch particles in a highly dispersed state.

The extreme turbulence which is maintained mechanically in the fluid layer by the bladed rotor prevents the very small drops of starch-modification agent from coalescing, favouring the completion of the desired reaction.

In fact, in connection with the completion of the starch-modification reaction, it should be noted that, according to the present invention, the reagents, (starch powder and agents for the chemical modification thereof) are no longer "dispersed" in an aqueous medium, but in an aeriform (or gaseous) medium of which the humidity is very low. The modification reaction achieved according to the method of the invention leads to the production, with a yield of practically 100%, of a reaction product (modified starch) which is constituted by a dry powder having a moisture content no greater than 25% by weight and does not involve the production of any aqueous reflux as occurred, on the other hand, with the methods of the prior art.

The method of the invention advantageously enables all of the starch-modification reactions currently

known to be carried out. In particular, it is possible to carry out acid hydrolysis of starch to various degrees, acetylation, etherification to produce valuable compounds such as methyl, ethyl, propyl, butyl starch, carboxymethyl starch, carboxyethyl starch, oxyethyl starch, oxypropyl starch, esterification, carboxylation by phosphorylation, and the like.

In particular, when used to hydrolyse starch, the method of the invention can be carried out with the use, as the starch-modification agent, of an aqueous solution of a strong acid which is nebulized mechanically upon admission to the turbo-reactor.

The strong acid used is preferably hydrochloric acid.

The method of the invention may advantageously be carried out with the use, as the starch-modification agent, of an alkylation agent selected from the group comprising C_{1-4} alkyl halides, C_{1-4} alkyl sulphates, halo- C_{2-4} -alkanoic acids, C_{2-4} alkylene epoxides.

Acylation agents such as those selected from the group comprising C_{2-4} acyl halides, anhydrides of C_{2-4} alkanolic acids and phosgene may effectively be used in the method of the invention.

If one of the aforementioned reactions requires the supply of heat (or the removal of heat) this can be achieved by the suitable heating (or cooling) of the internal wall of the turbo-reactor along which the thin, tubular, fluid layer of starch particles moves. For this purpose, the cylindrical, tubular body of the turbo-reactor will have one or more jackets through which a heating or cooling fluid is intended to flow.

The advantages and characteristics of the invention will become clearer from the following description of some examples of the implementation of the chemical starch-modification method, given below with reference to equipment shown schematically in the single appended drawing, which is provided purely by way of indication.

With reference to the drawing, equipment used for the chemical starch-modification method of the invention comprises a turbo-reactor constituted essentially by a cylindrical, tubular body 1, closed at its opposite ends by end plates 2, 3 and having a coaxial heating (or cooling) jacket 4 through which a fluid, for example, diathermic oil, is intended to flow to keep the internal wall of the body 1 at a predetermined temperature.

The tubular body 1 has openings 5, 6 for the admission of the starch to be modified chemically and of the modification agents used, respectively, as well as an opening 7 for the outlet of the chemically modified starch.

A bladed rotor 8 is supported for rotation in the tubular body 1, its blades 9 being disposed in a helical arrangement and being oriented for centrifuging and simultaneously transporting towards the outlet the reagents and the reaction products respectively.

A motor M is provided for driving the bladed rotor at speeds which may vary from 300 to 1500 revolutions/minute.

If the product (modified starch) discharged from the turbo-reactor requires further drying, the outlet opening

7 of the turbo-reactor communicates, by means of a duct 11, with the inlet opening 105 of a turbo-drier which is not described in detail since it has a structure just like that of the turbo-reactor mentioned above. The components of the turbo-drier which are similar to those of the turbo-reactor are indicated by the same reference numerals increased by 100.

EXAMPLE 1

A continuous flow of maize starch in powder form was supplied at a flow rate of 120 kg/h to the turbo-reactor 1 in which the bladed rotor 8 was rotated at a speed of 700 revolutions/minute and in which the internal wall was kept at a regulated temperature of about 50°. 25 kg/h of a 0.63% aqueous solution of hydrochloric acid was simultaneously supplied continuously through the opening 6.

Immediately upon admission to the turbo-reactor 1, the flow of starch powder was dispersed mechanically into starch particles which were immediately centrifuged against the internal wall of the turbo-reactor where they formed a thin, tubular and dynamic, fluid layer. At the same time, the aqueous solution of hydrochloric acid was mechanically nebulized finely by the blades of the rotor 8 which also immediately centrifuged the very small drops produced. These were thus introduced into the thin, tubular, fluid layer of starch particles with which they could "interact".

After a period of about 30 seconds spent in the turbo-reactor, an acid-modified starch which had a moisture content of 25% was discharged continuously from the opening 7.

This acid-modified starch was supplied continuously to the turbo-drier 13 together with a flow of hot air at a temperature of 160°C having the same direction of flow as the acid-modified starch.

The wall temperature in the turbo-drier 13 was regulated to a value of 120°C, whilst the speed of rotation of the bladed rotor was kept constantly at 900 revolutions/minute.

After 5 minutes spent in the turbo-drier, acid-modified starch having a relative moisture content of 11% was discharged continuously therefrom.

EXAMPLE 2

With the use of the equipment described schematically above and following the method of the invention, maize starch in powder form was supplied continuously into the turbo-reactor 1 through the inlet opening 5 at a flow rate of 120 kg/h. At the same time a 6.9% aqueous solution of NaOH was supplied continuously with the same direction of flow, at a flow rate of 2.5 kg/h, through the opening 6. Ethylene oxide was supplied to the same turbo-reactor 1 about half-way along the latter, with a flow rate of 95 kg/h, equal to 0.254 m³/h.

The wall temperature was regulated at a value of about 50°C, whilst the speed of rotation of the bladed rotor was kept constantly at 600 revolutions/minute.

After about 30 seconds spent in the turbo-reactor, oxyethylated starch with a degree of substitution of 0.1 was discharged continuously through the opening 7.

The oxyethylated starch was supplied continuously to the turbo-drier 13 where it was treated in the experimental conditions used in Example 1.

At the output of the turbo-drier, oxyethylated starch with a relative moisture content of 11% was obtained and was sent continuously through the duct 17 to a cyclone separator 18.

EXAMPLE 3

The method of Example 2 was repeated with the use of propylene oxide instead of ethylene oxide, all of the experimental conditions being kept unchanged.

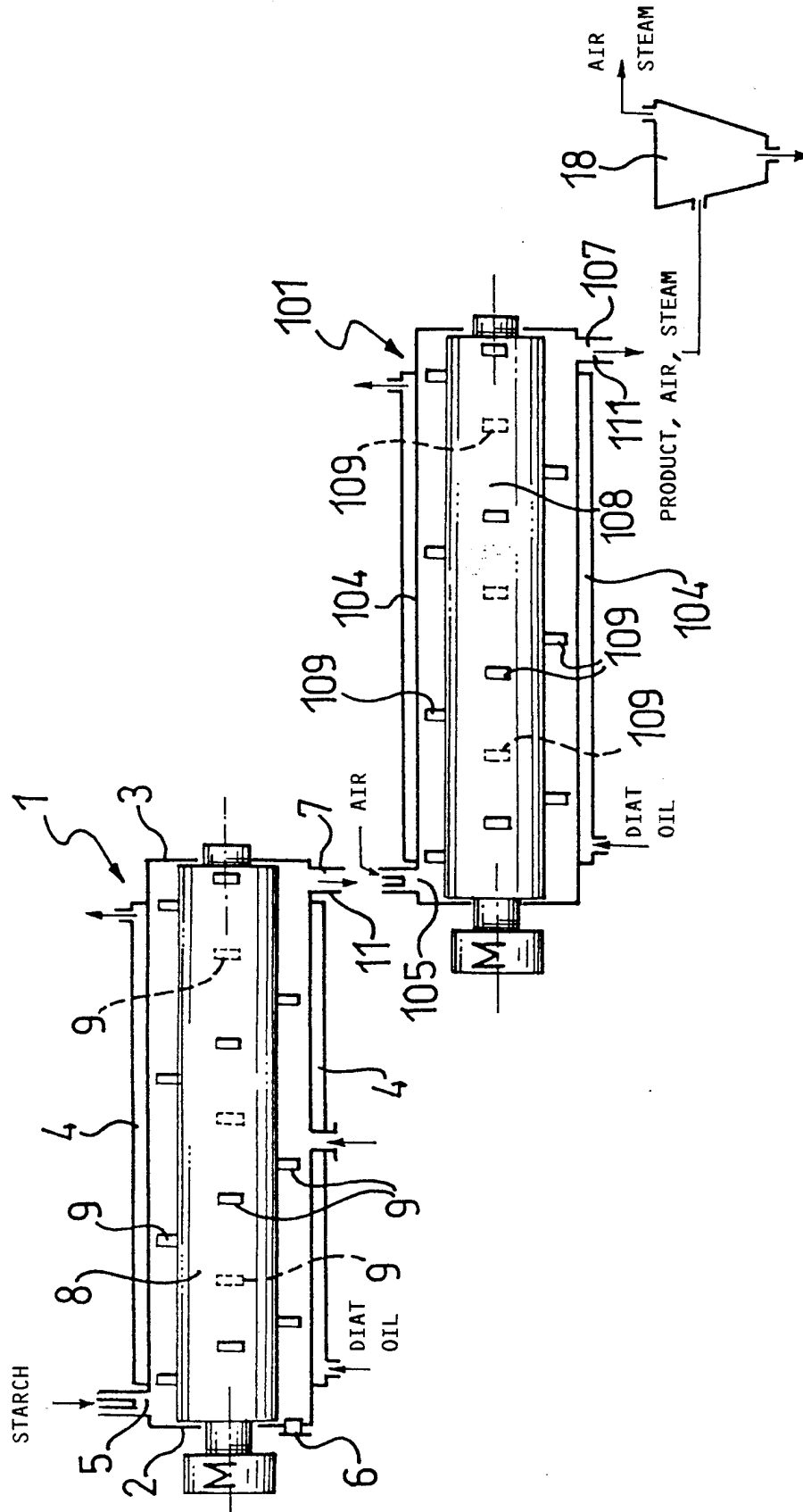
At the output of the turbo-reactor, oxypropyl starch was obtained with quantitative yields, having a degree of substitution of 0.1 and a relative moisture content of 25%. The oxypropyl starch was dried in the turbo-drier in the experimental conditions used in the previous examples, giving a final product having a relative moisture content of 11%.

Claims

1. A method for the continuous chemical modification of starch, characterized in that it comprises the steps of:
 - supplying a continuous flow of starch in powder form having a moisture content of between 9 and 25% into a turbo-reactor comprising a cylindrical, tubular body with a horizontal axis, having openings for the admission of agents and for the outlet of the final product, a bladed rotor supported for rotation in the cylindrical, tubular body, in which it is rotated at speeds within the range of from 300 to 1500 revolutions/minute, so as to disperse the continuous flow of starch into a flow of starch particles and, possibly a heating or cooling jacket for bringing the internal wall of the tubular body to a predetermined temperature,
 - supplying at least one continuous, substantially aeriform flow of at least one starch-modification agent into the turbo-reactor with the same direction of flow as the starch flow,
 - centrifuging the starch particles and the modification agent against the internal wall of the turbo-reactor forming a thin, tubular, dynamic, highly turbulent, fluid layer in which the starch particles and the modification agent are kept

mechanically in intimate contact by the blades of the bladed rotor, and

- reacting the starch and the agent in the thin layer whilst it advances substantially in contact with the internal wall towards the outlet opening of the turbo-reactor.
2. A method according to Claim 1, characterized in that the chemical starch-modification reaction product which is discharged from the turbo-reactor is subsequently dried in a turbo-drier.
 3. A method according to any one of Claims 1 and 2, characterized in that the at least one starch-modification agent is constituted by an aqueous solution of a strong acid which is nebulized mechanically upon admission to the turbo-reactor.
 4. A method according to Claim 3, characterized in that the strong acid is hydrochloric acid.
 5. A method according to any one of Claims 1 and 2, characterized in that the at least one starch-modification agent is constituted by an alkylation agent selected from the group comprising C₁₋₄ alkyl halides, C₁₋₄ alkyl sulphates, halo-C₁₋₄-alkanoic acids, and C₂₋₄ alkylene epoxides.
 6. A method according to any one of Claims 1 and 2, characterized in that the at least one starch-modification agent is constituted by an acylation agent selected from the group comprising C₂₋₄ acyl halides, anhydrides of C₂₋₄ alkanolic acids, and phosgene.





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EUROPEAN SEARCH REPORT

Application Number
EP 94 83 0524

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-3 527 606 (GERWIN G. TAYLOR ET AL.) * column 1, line 31 - line 33 * * column 2, line 5 - line 25 * * column 3, line 12 * ---	1-6	C08B31/00 C08B30/16
Y	EP-A-0 538 653 (VOMM IMPIANTI E PROCESSI) 28 April 1993 * page 2, line 39 - line 40 * ---	1-6	
Y	STARKE., vol.34, no.12, 1 December 1984, WEINHEIM DE pages 402 - 405 G.E.H. JOOSTEN ET AL. 'Some Aspects of the Continuous Production of Low-Acetylated Potato Starch' *page 403, column on the right, experimental 6 (c)* * page 405; figure 4 * ---	1-6	
A	US-A-4 216 310 (WURZBURG ET AL.) ---		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	US-A-3 114 656 (ROBERT L. OPILA) -----		C08B C13K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 March 1995	Examiner Lensen, H
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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DERWENT-WEEK: 200062

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TITLE: Continuous chemical modification of starch by centrifuging moisture contg. starch powder and continuous aeriform flow of starch-modification agent(s) within cylindrical turbo-reactor, creating thin tubular, dynamic, fluid layer

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PROCESSI SRL[VOMMN]

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1994BR-005269 (December 27, 1994)

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EP 710670 B1	June 14, 2000	EN
DE 69424942 E	July 20, 2000	DE
ES 2149251 T3	November 1, 2000	ES

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EP 710670A1	N/A	1994EP- 830524	November 3, 1994

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69424942E		624942	1994
EP 710670B1	N/A	1994EP-	November 3,
		830524	1994
BR 9405269A	Based on	1994BR-	December
		005269	27, 1994

INT-CL-CURRENT:**TYPE****IPC DATE****CIPS****C08B30/16 20060101****CIPS****C08B31/00 20060101****ABSTRACTED-PUB-NO: EP 710670 A1****BASIC-ABSTRACT:****A method for the continuous chemical modification of**

starch comprises: (i) supplying a continuous flow of starch in powder form having a moisture content of 9-25% into a turbo-reactor comprising a cylindrical tubular body with a horizontal axis, having openings for the admission of agents and for the outlet of final prod., a bladed rotor supported for rotation in the cylindrical body, in which it is rotated at speeds of 300-1500 revolutions/min to disperse the continuous flow of starch into a flow of starch particles and, possible a heating/cooling jacket to bring the internal wall of the reactor to predetermined temp.; (ii) supplying aeriform flow of starch-modification agent(s) into the reactor with the same direction of flow as the starch powder; (iii) centrifuging the starch particles and the modification agent(s) against the internal wall of the reactor to form a thin, tubular, dynamic, highly turbulent, fluid layer in which the starch and the modification agent are kept mechanically in intimate contact by the blades of the rotor; and (iv) reacting the starch and the agent in the thin layer whilst it advances in contact with the internal wall towards the

outlet opening of the reactor.

USE - Chemically modified starch is useful as raw material in industry, such as textile industry as sizing agent, paper industry for improving surface strength etc. and in food industry as gelling or thickening agents.

ADVANTAGE - The process can be adapted to carry out all known starch-modification reactions. The process can be carried out continuously, thereby improving control and economy of the reaction. Large quantities of aq. effluents are not produced, thus avoiding disposal problems.

TITLE-TERMS: CONTINUOUS CHEMICAL MODIFIED
STARCH CENTRIFUGE MOIST CONTAIN
POWDER AERIFORM FLOW AGENT
CYLINDER TURBO REACTOR THIN TUBE
DYNAMIC FLUID LAYER

DERWENT-CLASS: A11 D13 D17 F06 F09

CPI-CODES: A03-A; A10-E01; D03-H01J; D06-H01; F03-E01; F05-A06B; F05-A06C;

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Q9999 Q9347; K9392;
K9416; J9999 J2971
J2915; N9999 N6360
N6337; N9999 N6177*R;
N9999 N5812*R; N9999
N6439; N9999 N6780*R
N6655; N9999 N6359
N6337;

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R01704 9; G2335 D00
D64 D69 C* 4A O* 6A CI
7A R00365 221; H0226;

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